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Synthesis of ceria-praseodymia pigments by citrate-gel method for dental restorations

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Abstract

The objective of this paper was to synthesize both pure and praseodymia-doped ceria by using polymeric precursor method for their use as pigments for overlaying coating of dental ceramic restorations. These pigments were characterized by thermogravimetric and differential thermal analyses, X-ray diffraction, X-ray fluorescence, scanning electron microscopy, while UV–vis spectroscopy was used to determinate the reflectance curves of both pure and praseodymia-doped ceria. The referred pigments were added to feldspathic-glass frits in order to simulated the overlaying ceramic coatings on ceramic dental restorations. It was found to be a fluorescent coating by using the synthesized pure ceria but, a coating displaying a shade comparable to those of some commercial opaque layers when using praseodymia-doped ceria pigments with the lowest praseodymia content. Colorimetric coordinate measurements were carried out and used to plot the reflectance curves in the visible range for all types of the considered overlaying coatings.

Keywords: Pigments; Citrate-gel; Ceria; Praseodymia; Dental ceramic

1. Introduction

The studies on manufacturing of ceramic pigments have intensified lately once pigments are considered as an expensive raw material in the context of increasing volumes of new materials. Pigments are utilized in several applications: inks, plastics, rubbers, ceramics, enamels and glasses. However, the majority of inorganic pigments available for use are of toxic metals (cadmium, lead, chromium and cobalt). Therefore, researches for the application of rare-earth compounds have been intensified [1,2]. The applications of the rare-earths are due to their unique properties, mainly spectroscopic and magnetic ones [3].

The inorganic pigments are generally metallic oxides which possess chemical and high temperature stabilities, besides hardness and resistance to the attack from acids and alkalies, while presenting a suitable particle size distribution.

In the ceramic pigment domain, the concern is focused on high surface area powders, since this feature influences the color intensities and, therefore, there is a great interest on the development of nanosized pigments and among the processes available for synthesizing advanced ceramic raw materials, we may point out the polymeric precursor methods which lower the synthesis temperatures in the production of powder with nanosized particles [4].

In the particular case of Pechini method, a large amount of multi-element organometallic compound may exist dissolved in the organic matrix throughout the homogeneous organic resin formation process. This process is based on the formation of metal chelates between the metal cations and citric acid. These chelates undergo a polyestherification process when heated up in polyhydroxy-alcohol (resin formation, of ‘‘puff’’). Therefore the ions immobilized in chelates [5,6].

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The pure ceria may be used as dental porcelain pigment. However, its primary function is to simulate the natural fluorescence found in human tooth enamels [7,8].

Differently, the praseodymia-doped ceria pigments present shades from pink to orange and from red to brown in dental ceramic coatings and the color intensity depends on the praseodymia content in the ceria crystalline structure [9,10].

The combination of these synthesized pigments favours the reproduction of several kinds of human dental shades and thereby provides greater similarity between dental ceramic restorations to the natural teeth, under different light sources.

2. Materials and methods

A solution of citric acid ($C_6H_8O_7$, 99.50% from Vetec), 1 mol/l, was placed on a heating plate, under stirring, and after achieving 70 °C, 0.2 M aqueous solution of ($Ce(NO_3)_3 \cdot 6H_2O$, 99.00% from Sigma) was dropped till the completion of a 300 ml volume. Varying volume of a 0.05 M solution of hydrated praseodymium chloride ($PrCl_3 \cdot 6H_2O$, 99.90% from Aldrich) was dropped in order to provide the desired content of praseodymium in the final product. Ethylene glycol ($C_2H_6O_2$, 99.50%, from Vetec) was the last one to be added (24 ml) to the synthesis reactor. The temperature of the system was raised to 85 °C and maintained at this level under magnetic stirring during the formation of polymer ‘‘puff’’. The magnetic stirring was continued during the whole time necessary (6–8 h) to achieve the formation of ‘‘puff’’.

After ‘‘puff’’ formation, the magnetic stirrer was removed and a small amount of the ‘‘puff’’ was extracted for thermal analysis. The majority of the ‘‘puff’’ was kept inside the beaker and therein burnt at 500 °C for 4 h after heating up at a rate of 10 °C/min, followed by cooling down inside the furnace.

After cooling down to room temperature, the powder free from organics were disaggregated in the agate mortar and pestle and then calcined at 1000 °C for 2 h, after heating up at a rate of 10 °C/min.

Powder of pure ceria and 4 praseodymia-doped ceria were produced in order to increase the redness of the shade. Praseodymium of concentrations 1, 1.6, 3.3 and 5 mol% was used in the ceria–praseodymia mixtures.

The techniques used in the characterization of these synthesized pigments were as follows: X-ray fluorescence, X-ray diffraction, thermal analysis of the different ‘‘puffs’’ in order to determine the due temperature for the complete elimination of organics, scanning electron microscopy in order to observe the morphology of the particles and to get an insight into the particle size distribution, and thermal analysis of resultant pigments. The color measurements were carried out using a colorimeter in the CIELab space. This method allows the measurement of absorption intensity in the visible range in order to obtain L^* parameters, referring to brilliance [which varies from black (0) to white (100)], a^* which is the color intensity between red (+) and green (−), and b^* which is the color intensity between yellow (+) and blue (−). The values of L^*, a^* and b^* were collected by using different light sources for the pigment powders obtained.

The aqueous slip for coating sintered alumina plates was prepared by mixing the pigments into appropriate frit. The latter one was obtained by melting down a suitable feldspar (Table 1) with 20% borax (by weight) inside a platinum crucible, at 1100 °C for 2 h and then pouring the molten glass into water in order to provide fast cooling and to assure an amorphous structure.

The ceramic coatings were made up of 1 or 2 wt% of pigment and 98 or 99 wt% of frit, respectively, and organic binder (0.4 ml of CMC, 0.01 wt%). Only pigments of pure ceria and 1% praseodymium-doped ceria were used. This mixture was brushed onto the sintered alumina plate (Saint Gobain) substrate surface and the firing temperatures were 900 and 980 °C for 30 min (temperature utilized in prosthetic laboratories to coat dental restorations). Heating rate was 10 °C/min, while cooling rate was 20 °C/min. The values of L^*, a^* and b^* were collected by using a light source D65/2° and the curves of reflectance were drawn with them.

3. Results and discussions

The result of the thermogravimetric analysis of the ‘‘puff’’ showed a weight loss of 80%, typical of synthesis processes using polymeric precursor routes, while there occurred a greater weight loss in the temperature range around 500 °C (Fig. 1). With reference to the differential thermal analysis, one can observe three endothermic peaks, at values of 286, 304 and 337 °C, characteristic of thermal decomposition of estherified materials, with consequent elimination of CO_2 from polymeric chains bound to the metallic ions to form the oxides. Two exothermic peaks at 412 and 500 °C were found, which may be attributed to oxidation processes of the pure and praseodymia-doped ceria [11,12], and there was not any exothermic peak characteristic of crystallization above 500 °C. These results are confirmed by the evaluation of the derivative curve of the thermogravimetric analysis which showed the existence of two phenomena: one typical of polymeric decomposition reaction (once the peak corresponds to the endothermic curves of DTA) and the other characteristic of the ceria pigment formation (Fig. 1b) in the range around 400 °C. These results defined the firing temperature for the ‘‘puff’’ formation.

The X-ray diffraction peaks correspond to the fluorite structure cerium dioxide, even in samples doped with praseodymia, showing a satisfactory crystallinity due to the calcination temperature used (Fig. 2), since Casali et al. [4] studied the

Table 1
Composition of the feldspar

Substances	Concentration (%)	Substances	Concentration (%)
SiO_2	44.42	Rb_2O	0.04
Al_2O_3	12.80	MgO	0.81
CaO	24.51	Fe_2O_3	0.28
$K_2O + Na_2O$	7.34	MnO	0.09
TiO_2	0.08	SO_3	0.05
P_2O_5	8.75	SrO	0.06

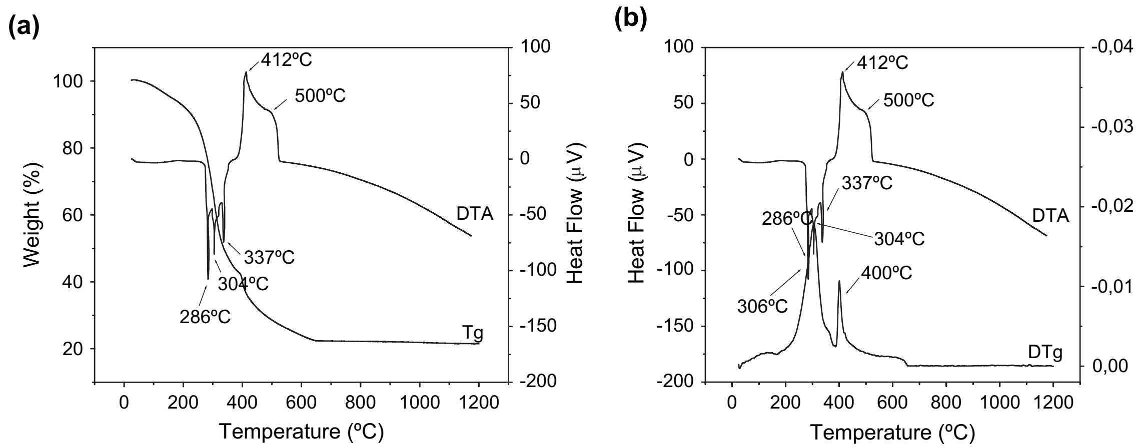

Fig. 1. Thermal analysis of the resin formed (''puff'') during the cerium (IV) oxide synthesis: (a) thermogravimetric analysis (TGA) and differential thermal analysis (DTA); (b) derivative of the thermogravimetric analysis (DTGA) and differential thermal analysis (DTA).

evolution of the crystalline phase as a function of temperature and found out that at 1000 °C the diffraction spectra presented the best definitions of the peaks for the doped ceria obtained by the Pechini method.

The results of the X-ray fluorescence analysis showed a short contamination with phosphorus and calcium oxides, but a high content of the desired oxide in the range around 99.40%. These same contaminations occurred in the production of this oxide doped with praseodymia and not interfered too on the yield, as seen in Table 2.

There was also consistency of pigments' shades, once pure ceria displayed as white changing to red upon addition of 1.6 mol% of praseodymium. A little bit more of praseodymia in the pigment composition provided intensification of the red shade. These results are confirmed by measured values from colorimetry which are presented in Table 3.

The value of L^* decreased from 91.37 to 67.49 with the addition of only 1.6 mol% of Pr, indicating a shade change from nearly white to one darker and this value decreased much more with further addition of Pr, achieving the value 45.07, a rather dark shade for the ceria pigment doped with 5 mol% Pr, under D65/2° light source. For each synthesized pigment, the values of the shades under two different light sources were measured (2° and 10°): and it can be observed that the decrease of L^* being proportional to the Pr content in all light sources used (Table 3). An inverse correlation for the a^* and b^* values is seen.

The values of a^* increased from −0.28 to 24.91 indicating that pigments with more red shades were achieved with the Pr content being increased from 0 to 5 mol%. Also, using the reflectance curve for the D65 light source, the absorption difference between pure ceria and ceria doped with praseodymia was observed, where occurred an intense reflectance along the full range of electromagnetic spectrum, as seen in Fig. 3, as opposed to the narrow reflectance range for ceria doped with praseodymia. The presence of praseodymium ion results into pigments which reflect red wavelength in the range from 600 to 700 nm.

The polymeric route for ceramic powder has received considerable attention lately because of its ability to provide pure oxides at lower temperatures, once the product resulting from pyrolysis of the polymeric resin is deaggregated and calcined at relatively low temperatures, giving rise to particle sizes in the nanometric ranges [6]. Therefore, the particles of the

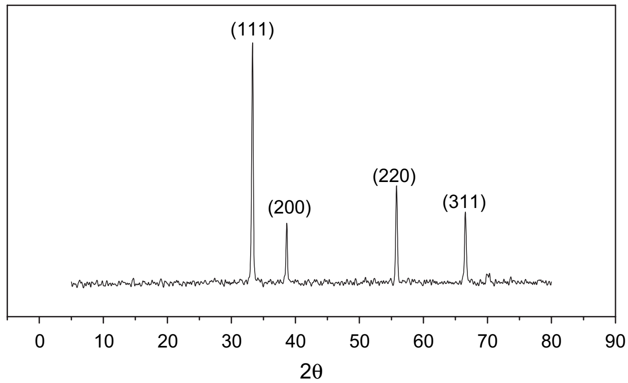

Fig. 2. X-ray diffraction of the ceria pigment synthesized by the Pechini method.

Table 2
Results of the chemical analyses accomplished by the technique of X-ray fluorescence for the pigments of pure ceria and doped with praseodymium

Pure ceria		Ceria + 1.6 mol% Pr	
Substances	Concentration (%)	Substances	Concentration (%)
CaO	0.10	CaO	0.08
CeO_2	99.40	CeO_2	97.90
Pr_2O_5	×	Pr_2O_5	1.60
P_2O_3	0.50	P_2O_3	0.43

Ceria + 3.3 mol% Pr		Ceria oxide + 5 mol% Pr	
Substances	Concentration (%)	Substances	Concentration (%)
CaO	0.09	CaO	–
CeO_2	96.51	CeO_2	96.51
Pr_2O_5	3.00	Pr_2O_5	4.91
P_2O_3	0.40	P_2O_3	0.46

Table 3
Colorimetric coordinates for pigments of pure ceria and doped with praseodymium (mol%) in different illuminants

Pigment	L^*				a^*				b^*			
	D65/2°	D65/10°	A/2°	A/10°	D65/2°	D65/10°	A/2°	A/10°	D65/2°	D65/10°	A/2°	A/10°
CeO_2	91.37	91.11	91.93	91.82	−0.28	0.16	2.84	2.90	10.04	10.27	9.88	10.37
1.6% of Pr	67.49	66.82	70.52	70.18	18.53	18.46	23.62	22.18	20.56	19.70	25.14	24.99
3.3% of Pr	55.36	54.74	58.70	58.38	22.31	21.58	27.25	25.18	17.99	17.74	24.08	23.78
5% of Pr	45.07	44.50	48.65	48.34	24.91	23.72	29.57	27.09	17.47	16.50	23.50	23.09

powders synthesized in this work displayed nanosizes, as can be seen in the scanning electron micrograph with amplification of an agglomerate of these nanosized ceria particles, where the smaller units observed are in the range of 100 nm (Fig. 4).

The production of fluorescent dental ceramics is important due to the use of blue wavelength emitting lamps, as ultraviolet radiation [13] in entertainment rooms. These lamps, when used in dancing rooms cause a white-blue fluorescence in human teeth [8]. Therefore, in dental restorations ceria coatings on the dental prosthesis surfaces are essential to provide this fluorescence and to guarantee this same effect as found in natural teeth under the considered light source [7]. It is possible to observe that the pure ceria coatings showed a trend to white-blue shades, once b^* values were small, indicating pale yellow and a^* values were small too and slightly negative, indicating a slight green shade. And L^* presented high values, indicating the white shade, as seen in Table 4. However, only by using the reflectance curve presented in Fig. 5, it is possible to prove that the ceramic coating containing pure ceria synthesized in this work possesses this fluorescence characteristics, once the light is emitted in the blue range of the electromagnetic spectrum.

In Table 4, one can observe the color shade values of the ceramic coating obtained in this work by using pure and 1 mol% praseodymium-doped ceria pigments. In the case of coatings containing praseodymia-doped ceria pigments, increased values of a^* and b^* were observed, indicating shade values tending to red and to yellow, respectively, and decreased values of L^*, indicating a some orange-like coating. These results are shown in Fig. 6, where the reflectance curves of the ceramic coatings with 1 and 2 wt% of the synthesized pigments of pure and 1 mol% praseodymium-doped ceria pigments presented different emitting ranges; pure ceria coating emitted in the blue range (better visualized in the scales of Fig. 6), and the 1 mol% praseodymium-doped ceria coatings presenting emission in the range of 550 nm (yellow) and 650 nm (red). In the case of praseodymia-doped ceria coatings, it may be said that they are used as pigments in ceramic coatings of dental restorations, once some layers utilized as opaque in commercial metal–ceramic restorations present shades similar to those obtained in this work, as displayed in Table 4, by the values of L^*, a^* and b^* of the coatings obtained using the pigments synthesized herein and two reflectances of commercial opaque, name ‘‘washopak’’ and ‘‘opak2m2’’, from Vita Zahnfabrik.

4. Conclusions

(1) It is confirmed that the decomposition of the polyestherification material occurred at around 350 °C and crystallization of the resulted oxides at about 500 °C; once above this temperature there was no characteristic exothermic peak.
(2) X-ray diffraction technique confirmed the presence of crystalline ceria, with short shifting of the strongest

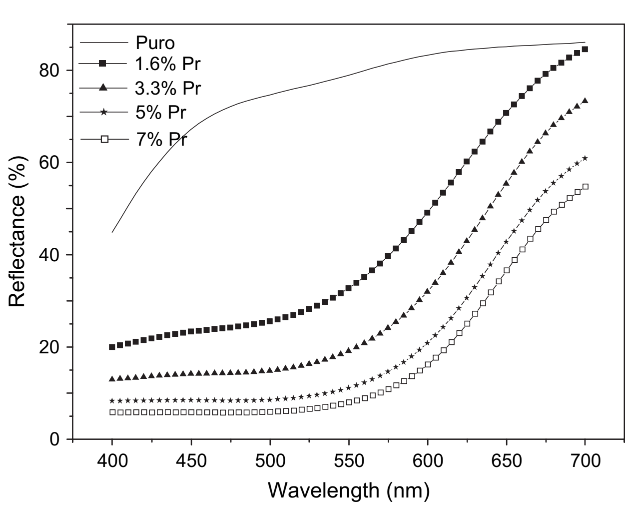

Fig. 3. Reflectances curves of synthesized pure and praseodymia-doped ceria pigments.

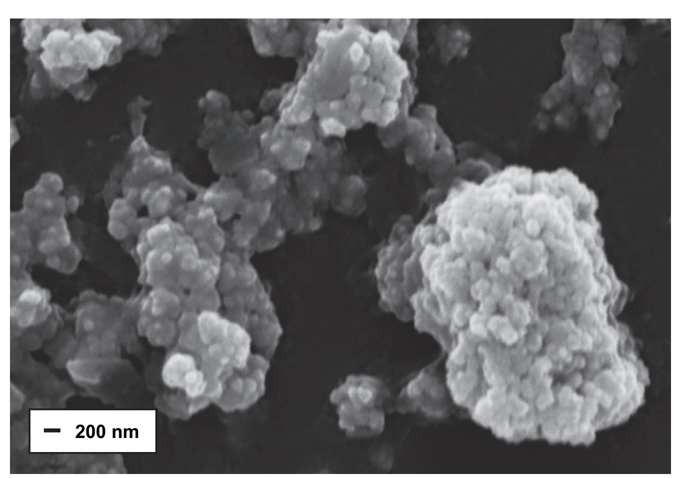

Fig. 4. Scanning electron micrograph image of pure ceria.

Table 4
Colorimetric coordinates of coatings with 1 and 2% of pure cerium oxide, 1 and 2% of cerium oxide doped with praseodymium (1 mol%) and two commercial references of the company Vita Zahnfabrik in illuminant D65/2°

Coatings	L^*	a^*	b^*
1% pure cerium oxide	91.78	−0.09	3.11
2% pure cerium oxide	91.84	−0.12	3.22
1% cerium oxide + Pr (1 mol%)	83.04	8.53	23.08
2% cerium oxide + Pr (1 mol%)	78.11	14.02	28.33
Commercial reference 1	75.62	9.87	33.76
Commercial reference 2	80.43	4.01	20.40

diffraction peaks with the increase of praseodymia content in the pigment, showing a doping (solid solution) instead of a crystalline mixture.

(3) The X-ray fluorescence technique showed a good yield in the synthesis of pure and praseodymia-doped ceria pigments and a small contamination with phosphorus and calcium.
(4) The increment in the praseodymia content provided a substantial change in reflectance characteristics of the synthesized pigments, once 1 mol% of Pr in the ceria conducted to a red-like pigment, with the reflectance restricted to the range of 600–700 nm, while the pure ceria presented intense reflectance in all range of the visible spectrum.
(5) The increase of praseodymia content in the pigment also provided an increase in the values of a^* and decrease of L^*, characteristic of the increase of red shade, both in the pure pigments and in the pigment containing ceramic coatings.
(6) The coating obtained from Brazilian mineral sources and pure ceria presented fluorescence, once light was emitted in the blue range of the electromagnetic spectrum.
(7) The ceramic coatings obtained with pigments containing 1 mol% Pr in ceria presented intense reflectances only in the restricted range from 600 to 700 nm, typical of ceramic samples with red shades. Theses coatings presented shades similar to those presented by commercial opaques from Vita Zahnfabrik.

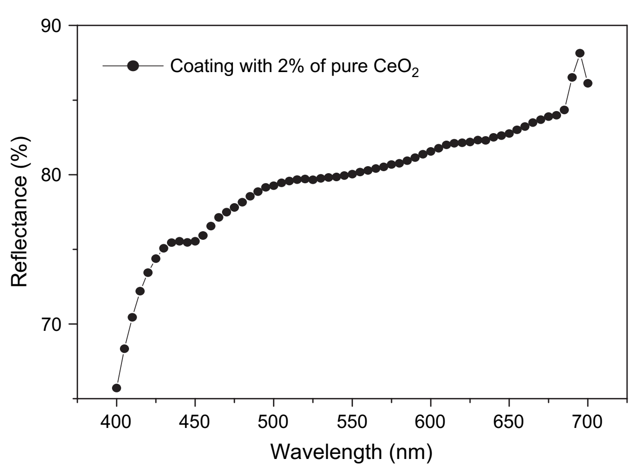

Fig. 5. Reflectance curve of the coating obtained with 2 wt% of pure ceria synthesized by using polymeric precursor method.

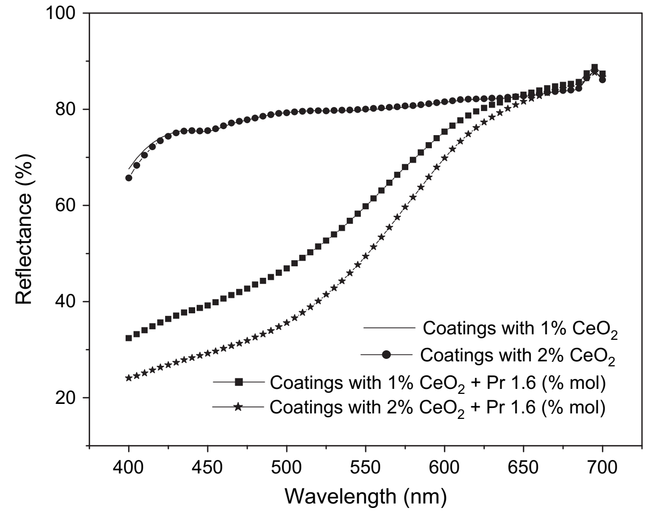

Fig. 6. Reflectance curves of the ceramic coating containing 1 and 2 wt% of the synthesized pure and 1 mol% Pr doped ceria pigments, using D65/2° light source.

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